

## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 05 April 2000 (05.04.00)	
<b>International application No.</b> PCT/KR98/00462	<b>Applicant's or agent's file reference</b>
<b>International filing date (day/month/year)</b> 24 December 1998 (24.12.98)	<b>Priority date (day/month/year)</b> 14 August 1998 (14.08.98)
<b>Applicant</b> LEE, Jung, Min et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

13 March 2000 (13.03.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

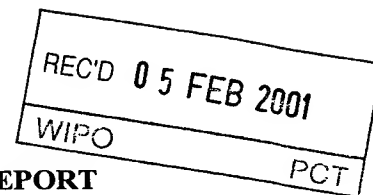
<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer</p> <p>Juan Cruz</p> <p>Telephone No.: (41-22) 338.83.38</p>
--	--

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)



Applicant's or agent's file reference	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/KR 98/00462	International filing date (day/month/year) 24 December 1998 (24.12.98)	Priority Date (day/month/year) 14 August 1998 (14.08.98)
International Patent Classification (IPC) or national classification and IPC IPC <sup>6</sup> : C 01 B 33/32, B 01 J 6/00		
Applicant KOREA RESEARCH INSITUTE OF CHEMICAL TECHNOLOGY et al.		

<p>1. This international preliminary examination report has been prepared by this International Preliminary Examination Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of <u>3</u> sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of _____ sheets.</p>
<p>3. This report contains indications relating to the following items:</p> <p>I <input type="checkbox"/> Basis of the report</p> <p>II <input type="checkbox"/> Priority</p> <p>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p>IV <input type="checkbox"/> Lack of unity of invention</p> <p>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p>VI <input type="checkbox"/> Certain documents cited</p> <p>VII <input type="checkbox"/> Certain defects in the international application</p> <p>VIII <input type="checkbox"/> Certain observations on the international application</p>

Date of submission of the demand 13 March 2000 (13.03.00)	Date of completion of this report 14 December 2000 (14.12.00)
Name and mailing address of the IPEA/AT Austrian Patent Office Kohlmarkt 8-10 A-1014 Vienna Facsimile No. 1/53424/200	Authorized officer Pamminger Telephone No. 1/53424/223

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/KR 98/00462

## I. Basis of the report

1. With regard to the elements of the international application:\*

☒ the international application as originally filed

☐ the description:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☐ the claims:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, as amended (together with any statement) under Article 19

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☐ the drawings:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

☐ the sequence listing part of the description:

pages \_\_\_\_\_, as originally filed

pages \_\_\_\_\_, filed with the demand

pages \_\_\_\_\_, filed with the letter of \_\_\_\_\_

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

☐ the language of publication of the international application (under Rule 48.3(b)).

☐ the language of the translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☐ The amendments have resulted in the cancellation of:

☐ the description, pages \_\_\_\_\_

☐ the claims, Nos. \_\_\_\_\_

☐ the drawings, sheets/fig \_\_\_\_\_

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\*

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as „originally filed“ and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.  
PCT/KR 98/00462

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Claims	1-6	YES
	Claims		NO
Inventive step (IS)	Claims	1-6	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-6	YES
	Claims		NO

### 2. Citations and explanations (Rule 70.7)

**D1 = EP 2 638 154 A1**

**D2 = EP 293 640 A2**

(See Search Report)

It is obvious that neither **D1** nor **D2** describes the special methode for manufacturing crystalline layered sodium disilicate according to claim 1 of the application. Claim 1 is new.

Claims 2 - 6, which are concerning further embodiments of subject matters of claim 1 are also new.

In summary we can state that all the claims are fullfilling the requirements of novelty, inventive step and industrial applicability.



W

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>7</sup> :</b> <b>C01B 33/32, B01J 6/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 00/09444</b> <b>(43) International Publication Date:</b> 24 February 2000 (24.02.00)
<b>(21) International Application Number:</b> PCT/KR98/00462 <b>(22) International Filing Date:</b> 24 December 1998 (24.12.98) <b>(30) Priority Data:</b> 1998/32993 ✓ 14 August 1998 (14.08.98) KR <b>(71) Applicant (for all designated States except US):</b> KOREA RE-SEARCH INSTITUTE OF CHEMICAL TECHNOLOGY [KR/KR]; 100, Jang-dong, Yusung-ku, Daejeon 305-343 (KR). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> LEE, Jung, Min [KR/KR]; 383-22, Doryong-dong, Yusung-ku, Daejeon 305-340 (KR). SUH, Jeong, Kwon [KR/KR]; 136-906, Hanbit Apt., Uheun-dong, Yusung-ku, Daejeon 305-333 (KR). JEONG, Soon, Yong [KR/KR]; 113-603, Nuri Apt., Weolpyung-dong, Seo-ku, Daejeon 302-280 (KR). PARK, Chun, Hee [KR/KR]; 25-501, Misung Apt., Apgujung-dong, Kangnam-ku, Seoul 135-110 (KR). PARK, Jeong, Hwan [KR/KR]; 107-203, Mujikae Apt., Weolpyung-2dong, Seo-ku, Daejeon 302-282 (KR). KIM, Jong, An [KR/KR]; 3-204, Sujeong Apt., 909, Doonsan-2dong, Seo-ku, Daejeon 302-173 (KR).		<b>(74) Agent:</b> HUH, Sang, Hoon; Hyecheon Building, 13th floor, 831, Yeoksam-dong, Kangnam-ku, Seoul 135-792 (KR).  <b>(81) Designated States:</b> CN, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> AN IMPROVED METHOD FOR MANUFACTURING CRYSTALLINE LAYERED SODIUM DISILICATE		
<b>(57) Abstract</b> <p>The present invention relates to an improved method for manufacturing a crystalline layered sodium disilicate and more particularly, to the improved method for manufacturing the crystalline layered sodium disilicate comprising the steps including the preparation of granules in a certain ratio of anhydrous sodium silicate cullet, a starting material, in the presence of some binders such as water and an aqueous solution of sodium silicate, followed by a crystallization step of the granules, thus ensuring that a small amount of final product is recycled to the prior crystallization step in order to prevent the attachment of granules to an inner crystallization device, which occurs due to local sintering in a high-temperature crystallization condition of continual process and also to further enhance the unit productivity during the mass production of crystalline layered sodium disilicate.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

# AN IMPROVED METHOD FOR MANUFACTURING CRYSTALLINE LAYERED SODIUM DISILICATE

## BACKGROUND OF THE INVENTION

### 5 Field of the Invention

The present invention relates to an improved method for manufacturing a crystalline layered sodium disilicate and more particularly, to the improved method for manufacturing the crystalline layered sodium disilicate comprising the steps including the preparation of granules in a certain ratio of anhydrous sodium silicate cullet, a starting material, in the presence of some binders such as water and aqueous solution of sodium silicate, followed by a crystallization step of the granules, wherein a small amount of final product is recycled to the prior crystallization step in order to prevent the attachment of granules to an inner crystallization device, which occurs due to local sintering in a high-temperature crystallization condition of continual process and also to further enhance the unit productivity during the mass production of crystalline layered sodium disilicate.

### Description of the Related Art

20 The term "cullet" used as a starting material of this invention, which has been frequently used as a raw material in a field involved in the manufacture of sodium silicate solution, refers to a compound in a small lump or piece derived from amorphous sodium silicate, prepared in such a manner that a mixture of silica and sodium carbonate in an appropriate molar ratio (ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$ , namely  $\text{SiO}_2/\text{Na}_2\text{O}$ ) is heated at the temperature of 25  $1000-1400^\circ\text{C}$ , melted and cooled.

In addition, the term "layered sodium silicate" refers to crystalline silica compounds expressed by " $(\text{Na}_2\text{O})_x(\text{SiO}_2)_y$ " (where  $y/x$  varies differently

depending on the crystal structure and has the common values ranging from 2 to 11); among them, the crystalline layered sodium silicate expressed by  $\text{Na}_2\text{Si}_2\text{O}_5$  is reported to have various crystal forms such as  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ -phases, and with its excellent adsorptivity and ion-exchange capacity originated from structural specificity, the crystalline layered sodium disilicate has been useful as a catalytic carrier or in a variety of chemical processes such as separation and purification. With its higher binding capacity on the hardness components in water such as  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in particular, the crystalline layered sodium disilicate in  $\delta$ -phase, the crystalline layered sodium disilicate has been recently used as a water softener or detergent composition builder.

However, the process for manufacturing the crystalline layered sodium disilicate in  $\delta$ -phase has recognized some disadvantages in that severe foaming induced by a leakage of remaining water is generated in the initial crystallization step, and with sintering and shrinkage of particles, they are deposited in the crystallization device.

To comply with this matter, U.S. Patent No. 5,211,930 has added a method for recycling 10-50wt% of final product to the crystallization step, thus preventing deposit of products in a calcination device.

However, the above method has proven to be uneconomical with poor unit productivity during mass production, since a large amount (10-50wt%) of final product is recycled to the device; the reduction of unit productivity cannot be overcome in a process where powders containing a large amount of water is fed.

Under such circumstances, in an effort to prevent the deposits of final product in the crystallization device, the inventor et al. in their respective patents (U.S. Patent No. 5,567,404, its corresponding Korea Patent No. 139976 and Korea Patent Appln. No. 97-33207) have disclosed some methods for

manufacturing the crystalline layered sodium disilicate in such a manner that water or aqueous solution of sodium silicate in a small amount for agglomeration is added to a cullet powder, a starting material, thereby preparing granules with a small amount of water and then the granules are  
5 crystallized in calcination furnace, thus ensuring more simplification of manufacturing process, reduction in energy consumption, and removal of deposits remaining in the device. Notwithstanding this, these methods have still failed to eliminate the deposits of some granules in the device during the crystallization step, when a continual process for mass production is operated.

10

## SUMMARY OF THE INVENTION

To overcome the aforementioned shortcoming that reactants are deposited in a crystallization device, the inventor et al. have found that a process recycling a small amount of final product to the device may not only  
15 eliminate the deposit of product in a calcination furnace associated with local sintering occurring at a higher temperature during continual process, but also recycle less amount than that of the U.S. Patent No. 5,211,930, thus resulting in significant increase of unit productivity during mass production. In consequence, the inventor et al. have completed this invention.

20 Therefore, an object of this invention is to provide an improved method for manufacturing a crystalline layered sodium disilicate, being characterized in that some defects found in the crystallization device have been completely removed by specifying the agglomeration and recycling steps for possible continual process, thereby improving unit productivity during  
25 mass production.

## Detailed Description of the Invention

This invention is characterized by an improved method for

manufacturing crystalline layered sodium disilicate comprising the subsequent steps of a) preparing granules with the addition of water as binder to anhydrous sodium silicate cullet powder; b) drying and crystallizing the granules by heat calcination to prepare sodium disilicate, wherein 3-5wt% of  
5 final product, sodium disilicate, is recycled to the prior crystallization step.

Also, this invention is characterized by an improved method for manufacturing the crystalline layered sodium disilicate comprising the subsequent steps of a) preparing granules with the addition of an aqueous solution of sodium silicate as binder to anhydrous sodium silicate cullet  
10 powder; b) drying and crystallizing the granules by heat calcination to prepare sodium disilicate, wherein 3-5wt% of final product, sodium disilicate, is recycled to the prior crystallization step.

This invention is explained in detail as follows:

This invention relates to a method for manufacturing a crystalline  
15 layered sodium disilicate, performed in such subsequent steps that a certain amount of water or aqueous solution of sodium silicate is added to an anhydrous sodium silicate cullet powder comprising a certain ratio of chemical composition for the preparation of granules, followed by drying and calcining for their crystallization, wherein a step of recycling some final  
20 products to the crystallization device has contributed much to settlement of several problems associated with the continual operation, since the recycling process makes it possible to separate the reactants, which may be sintered in the device at a high temperature (500-800°C), from inner wall of the crystallization device. According to this invention, the recycling step of final  
25 product in small amounts is available in that from the step of preparing granules, the round-form agglomeration may minimize the contact area in the crystallization device.

As described in the respective patents (U.S. Patent No. 5,567,404, its

corresponding Korea Patent No. 139976 and Korea Patent Appln. No. 97-33207) disclosed by the inventor et al., the agglomeration step highlighted by this invention, which has several advantages in that a) unlike the conventional method with crystallization process for powder material, high-density materials supplied to crystallization device may cause no dust with a higher unit productivity; b) minimization of contact area with the device due to agglomeration may significantly prevent any attachment caused by the sintering of reactants. However, the manufacturing method using the agglomeration step has failed to efficiently prevent the attachment of reactants to the inner wall of calcination device during mass production of continual operation.

To efficiently prevent the attachment of granules to the device, a small amount of final product (less than 5wt%) is recycled to separate the reactants sintered from inner wall of the crystallization device.

The process for manufacturing a crystalline layered sodium disilicate of this invention is briefly illustrated in Fig. 1 and each process step is explained in more detail as follows:

First, a cullet (the molar ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  is 1.80-2.20) is pulverized to make a cullet powder having less than 0.8 mm ( $D_{50} \approx 0.3$  mm) in its particle size;

Second, water and aqueous solution of sodium silicate (the molar ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  used as a binder is 2.0-3.3, solid content: 15-40wt%) is added to the cullet powder to prepare a granule having 1-30mm (volumetric density: 1.1-1.6g/cm<sup>3</sup>) in its diameter; hence, the water used for the agglomeration of cullet powder acts not only as a binder, but also as an indispensable component for the phase transfer due to hydration. In view of the fact that the manufacturing conditions for granules vary differently depending upon the amount of water, water may be directly used but the use of aqueous solution

of sodium silicate may enhance the adhesive power of solid component in the binder composition of cullet powder, thus making it easier to adjust the amount of water.

It is preferred that 5-30wt% of water is added to an anhydrous sodium silicate cullet powder, when water is directly used as a binder. Further, it is preferred that an aqueous solution of sodium silicate containing 15-40wt% of solid component is used as a binder for the adjustment of water contents; the amount of sodium silicate in aqueous solution is in the range of 10-30wt% to the anhydrous sodium silicate cullet powder.

Hence, the agglomeration device includes any type of agglomeration device such as a round type, a cylindrical type, fluidized type and molding press.

Then, the step of drying the granules is performed, followed by calcination to finally prepare the crystalline layered sodium disilicate.

According to this invention, granules are subjected to a drying step before it is delivered to a continual calcination device, since such drying step may effectively prevent the combining of granules induced by the adhesiveness of aqueous solution of sodium silicate present in the surface of granules, while making it easier not only to deliver the granules, but also to form the phase variation during crystallization by facilitating the hydration in the granules.

However, the drying step at extremely high temperature is responsible for generation of any impurities, thus reducing the purity of final product. In this respect, it is preferred that the drying step is performed at 80-200°C until the amount of evaporated water becomes 0.2-1.0wt%. The volumetric density of the granules, so dried, should be maintained at 1.1-1.6g/cm<sup>3</sup>.

The granules are placed at a rotary calcination furnace, crystallized for 0.1-1 hour at 650-800°C to form a material with 0.1-0.5g/cm<sup>3</sup> of volumetric

density, and pulverized with a crusher.

Meantime, the recycling step highlighted by this invention is to re-supply some of final product to a crystallization device, together with dried granules. Hence, the particle size of final product for recycling is of little significance but the step of recycling some micropowders may cause the occurrence of dusts, which will result in heavy load to a bag filter during continual operation. Therefore, it is preferred that the particle size of final product for recycling is in the range of 0.2-1.0mm ( $D_{50} \approx 0.6 \text{ mm}$ ).

The recycling step using a larger amount of final product is advantageous in preventing any attachment or formation of mass in the device but this may adversely affect the unit productivity. To achieve the objective of this invention, therefore, a priority should be given to the limitedness of the recycling amount of final product. Therefore, the recycling amount of final product is less than 5 wt% at maximum in proportion to the total amount of granule, preferably 3-5 wt%. Hence, if the recycling amount is less than 3 wt%, a sintering occurs in some granules which are momentarily attached to or detached from the inner wall of a calcination furnace, or a mass of granules is formed or sintered. At this time, the  $\alpha$ -type crystal phase occurs partially in the final product.

Further, if the recycling amount of final product exceeds 5 wt%, the individual rotation of granules impedes their swift delivery, when contacted with an excessive recycling amount of final product during the crystallization. Under such circumstances, any retention time of granules cannot be constantly maintained in addition to possible occurrence of dusts and furthermore, the unit productivity becomes significantly reduced thereto.

As such, the product prepared by recycling an appropriate amount of final product exhibits an excellent physical property as a  $\delta$ -phase crystalline layered sodium disilicate in high purity.

The salient points relating to the process for manufacturing a crystalline layered sodium disilicate of this invention may be summarized as follows:

First, the homogeneous crystallization of granules may be ensured by recycling a small amount of final product together with granules, and the coagulation of granules and the inner wall of the device due to local sintering during crystallization may be prevented by the recycling powder.

Second, since the attachment of granules in the device may be prevented, the continual process is available and by recycling a small amount of final product, a higher unit productivity may also lead to an optimization of the process thereto.

This invention is explained in more detailed based on the following examples but is not limited by these examples.

#### Example 1

5kg of a cullet powder (molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ : 2.03, particle size:  $D_{50} \approx 0.3$  mm) was placed at a hopper for raw material, and transferred to a round-type agglomeration device at a speed of 60g/min ( $\phi 40$  cm, Yongjin Machinery Co. of Korea). While rotating the material at 15 rpm with an angle of inclination at  $48^\circ$ , aqueous solution of silicate sodium having the molar ratio of 2.26 in  $\text{SiO}_2/\text{Na}_2\text{O}$  (solid content: 30 wt%, Shinhoong Silicate Product of Korea) was added dropwise at 13g/min to give granules. Then, the granules in round form having about 8 mm in its average diameter were continuously obtained.

The granules dried by a air flow oven at  $120^\circ\text{C}$  for 30 mins (amount of evaporated water: 0.5 wt%, volumetric density:  $1.31 \text{ g/cm}^3$ ), were placed at a hopper for raw material in a rotary calcination furnace ( $\phi 20$  cm  $\times$   $\ell$  300 cm, Dong-A Heavy Industries of Korea), and transferred to a calcination furnace

(feeding rate by a vibration feeding device: 200g/min) at 725°C, together with the amount, indicated in Table 1, of final pulverized product for recycling at a speed of 6g/min. Hence, the reactant was crystallized at the retention time of 20 mins with the angle of inclination at 0.5 ° and at 8 rpm.

5           During such crystallization, any attachment of reactant to the inner device was not observed. Then, a whitish porous crystalline layered sodium disilicate with the expanded volumetric density of about 0.26g/cm<sup>3</sup> was obtained, while keeping the initial granule form via appropriate rotational operation of individual granules.

10

### Example 2

          The granules prepared in the same manner as Example 1 was transferred to a calcination furnace at a speed of 200 g/min, together with the amount, indicated in Table 1, of final pulverized product for recycling at a  
15   speed of 10g/min. Then, a crystalline layered sodium disilicate was prepared in the same manner as Example 1. During such process, any attachment of reactant to the inner device was not observed.

### Comparative example 1

20           The granules prepared in the same manner as Example 1 were transferred to a calcination furnace at a speed of 200 g/min, while any final product for recycling was not added. Then, a crystalline layered sodium disilicate was prepared in the same manner as Example 1. During the manufacturing process, some reactants was momentarily sintered and  
25   attached to an inner wall of calcination device. The formation of mass or attachment among some granules were observed.

### Comparative example 2

The granules prepared in the same manner as Example 1 were transferred to a calcination furnace at a speed of 200 g/min, together with the amount, indicated in Table 1, of final pulverized product for recycling at a speed of 20g/min. Then, a crystalline layered sodium disilicate was prepared in the same manner as Example 1. Dusts were generated in the process of supplying the raw materials and individual rotation of granules were insufficiently made due to recycling of final product in excess amount.

#### **Experimental example 1: Attachment of granules in the calcination device**

The attachment of granules in the calcination device was observed with naked eye at the tube end of crystallization device. The results were shown in the following Table 1.

#### **Experimental example 2: Measurement for the binding capacity of final product to hardness component**

The final products prepared from Examples 1-2 and Comparative example 1-2 was pulverized by ball-mill for 30 minutes and classified to make the particle size of 43-104  $\mu\text{m}$ . Then, the binding capacity to  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  was measured in the following manner.

20

##### **(1) Measurement for the binding capacity to $\text{Ca}^{2+}$**

About 1.0g of sample was weighed, transferred to a stirrer at 25°C and then, 1000 ml of hard water (aqueous solution of  $\text{Ca}^{2+}$ , hardness: 200mg $\text{Ca}^{2+}$ /l) was added to the sample. The mixture was stirred for 15 minutes and filtered off immediately. 25ml of the remaining solution, accurately collected, was transferred to a 100ml Erlenmeyer flask, followed by the addition of 2-3 ml of  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution (pH 10). E.B.T indicator was added to the mixture, and titrated with a standard solution of 0.01M EDTA. Then, the

binding capacity to  $\text{Ca}^{2+}$  was calculated using the following equation 1.

**Equation 1.**

5 Binding capacity to  $\text{Ca}^{2+}$  ( $\text{mgCa}^{2+}/\text{g}$ ) =  $[12.5 - (t \times f)/w] \times (200/12.5)$

Where, t is a consumption amount of EDTA (ml); w is a weight of sample(g); and f is a factor of EDTA solution used.

(2) Measurement for the binding capacity to  $\text{Mg}^{2+}$

10 About 1.0g of sample was weighed, transferred to a stirrer at  $25^{\circ}\text{C}$  and then, 1000 ml of hard water ( $\text{Mg}^{2+}$  solution, hardness:  $120 \text{ mgCa}^{2+}/\ell$ ) was added to the sample. The mixture was stirred for 15 minutes and filtered off immediately. 25ml of the remaining solution, accurately collected, was transferred to a 100ml Erlenmeyer flask, followed by the addition of potassium  
15 cyanide solution (10%) 0.5 ml, several drops of hydroxychloride ammonium solution (10%) and 2-3 ml of  $\text{NH}_3\text{-NH}_4\text{Cl}$  buffer solution (pH 10). E.B.T indicator was added to the mixture, and titrated with a standard solution of 0.01M EDTA. Then, the binding capacity to  $\text{Mg}^{2+}$  was calculated using the following equation 2.

20 **Equation 2.**

Binding capacity to  $\text{Mg}^{2+}$  ( $\text{mgMg}^{2+}/\text{g}$ ) =  $[12.5 - (t \times f)/w] \times (120/12.5)$

Where, t is a consumption amount of EDTA (ml); w is a weight of sample(g); and f is a factor of EDTA solution used.

Table. 1

Category	Product for recycling		Attachment in calcination device	Binding capacity in terms of hardness	
	Recycling amount (wt%)	Average particle size(D50, $\mu\text{m}$ )		$\text{Ca}^{2+}$ ( $\text{mg Ca}^{2+}/\text{g}$ )	$\text{Mg}^{2+}$ ( $\text{mg Mg}^{2+}/\text{g}$ )
Examp. 1	3	0.6	Not attached	109.7	91.2
Examp. 2	5	0.6	Not attached	112.5	92.4
Comp. examp. 1	0	-	Attached partially or mass-formed	97.3	76.7
Comp. examp. 2	10	0.6	Not attached but unavailable in swift rotation	107.3	89.2

As mentioned above, this invention relates to a method for manufacturing the crystalline layered sodium disilicate comprising the steps including the preparation of granules from an anhydrous sodium silicate cullet with the addition of some binders such as water and aqueous solution of sodium silicate, followed by a crystallization process of the granules, thus ensuring that a small amount of final product is recycled to the prior crystallization step in order to prevent the attachment of granules to an inner crystallization device, which occurs due to local sintering in a high-temperature crystallization condition of continual process and also to further enhance the unit productivity during the mass production of crystalline

layered sodium disilicate. Further, the crystalline layered sodium disilicate prepared by this invention has an excellent physical property, when the granules are crystallized.

## CLAIMS

What is claimed is:

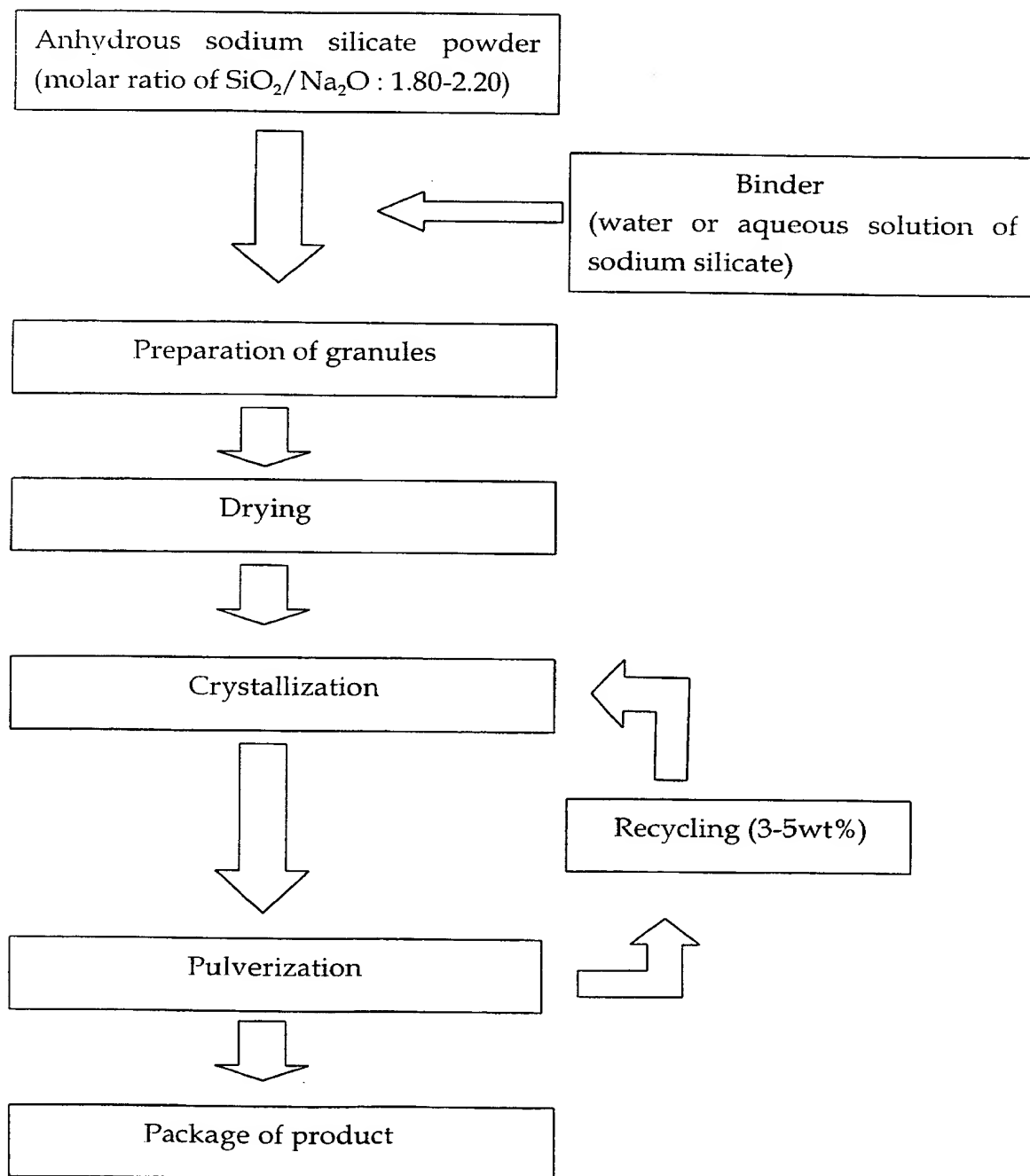
1. A process for manufacturing crystalline layered sodium disilicate comprising the steps of a) preparing granules with the addition of water as binder to anhydrous sodium silicate cullet powder; and b) drying and crystallizing the granules by calcination to prepare sodium disilicate, wherein 3-5wt% of final product, sodium disilicate, is recycled to the prior crystallization step.
2. The process for manufacturing crystalline layered sodium disilicate according to claim 1, wherein the water as said binder component is added to the anhydrous sodium silicate cullet powder in the range of 5-30 wt%.
3. The process for manufacturing crystalline layered sodium disilicate according to claim 1, wherein the crystallization step is performed at 650-800°C.
4. A process for manufacturing crystalline layered sodium disilicate comprising the steps of a) preparing granules with the addition of an aqueous solution of sodium silicate as binder to anhydrous sodium silicate cullet powder; and b) drying and crystallizing the granules by calcination to prepare sodium disilicate, wherein 3-5wt% of final product, sodium disilicate, is recycled to the prior crystallization step.
5. The process for manufacturing crystalline layered sodium disilicate according to claim 4, wherein an aqueous solution of sodium silicate as said binder component (molar ratio of  $\text{SiO}_2/\text{Na}_2\text{O}$ : 2.0-3.3, solid content: 15-40 wt%) is added to the anhydrous sodium silicate cullet powder in the range of 10-30

wt%

6. The process for manufacturing crystalline layered sodium disilicate according to claim 4, wherein the crystallization step is performed at 650-800 °C.

## FIGURE

FIG. 1



# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR 98/00462

## A. CLASSIFICATION OF SUBJECT MATTER

IPC<sup>7</sup>: C 01 B 33/32, B 01 J 6/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup>: C 01 B 33/32; B 01 J 6/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 638 154 A1 (AUSIMONT S.R.L.), 18 October 1989 (18.10.89), claims.	1,4
A	EP 0 293 640 A2 (HOECHST AKTIENGESELLSCHAFT), 07 December 1988 (07.12.88), claims.	1,4
	----	

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

\* Special categories of cited documents:

„A“ document defining the general state of the art which is not considered to be of particular relevance

„E“ earlier application or patent but published on or after the international filing date

„L“ document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

„O“ document referring to an oral disclosure, use, exhibition or other means

„P“ document published prior to the international filing date but later than the priority date claimed

„T“ later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

„X“ document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

„Y“ document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

„&“ document member of the same patent family

Date of the actual completion of the international search

13 September 1999 (13.09.99)

Date of mailing of the international search report

28 September 1999 (28.09.99)

Name and mailing address of the ISA/AT  
Austrian Patent Office  
Kohlmarkt 8-10; A-1014 Vienna  
Facsimile No. 1/53424/200

Authorized officer

Pamminger

Telephone No. 1/53424/223

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR 98/00462

**FR 2 638 154 A** describes a 2- stage process for the prodn. of compact, granular, non-clumping, water soluble sodium silicate of molar ratio 1.6 - 3.5  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$ . In the first stage an aq. soln. containing 30-60 wt.% of the desired silicate is heated to 130 - 170 °C in a rotating drum in the presence of recycled dried prod. until the water content of the intermediate prod. is 10-15 wt.% and its apparent density is 0.1 - 0.3 kg/l. In the second stage the intermediate prod. is densified to an apparent density of above 0.9 kg/l and a water content of 15-20 wt.% by the addn. of 20-35 pts. wt. of the original soln. to 100 pts. wt. intermediate prod. whilst heating to 80-100 deg.C in a second rotating drum.

**EP 293 640 A2** describes crystalline sodium silicates with a layered structure and a  $\text{SiO}_2$ :  $\text{Na}_2\text{O}$  mol. ratio of 1.9-3.5:1 are prepd. from water glass solns. of 20-65 wt.% solids content by spray drying to form pulverulent amorphous sodium silicate with max. 20 wt.% loss on ignition, the waste gas leaving the spray drying zone, being at least 140 °C; and firing in a moving bed zone at 500-800 deg.C for 1-60 mins. in the presence of at least 10 wt.% recycled material obtd. by crushing the crystalline sodium silicate discharged from the firing zone.

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

PCT/KR 98/00462

In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
FR A1 2638154	27-04-1990	BE AD 1002871 ES AF 2020029 FR B1 2638154 IT AO 8822383 IT A 1230579	09-07-1991 16-07-1991 10-01-1992 21-10-1988 28-10-1991
EP A2 293640	07-12-1988	AT E 73737 CA A1 1334619 DE A1 3718350 DE CO 3869209 DK AO 2954/88 DK A 2954/88 DK E1 167917 EP A3 293640 EP B1 293640 ES T3 2031175 JP A2 63310717 JP B4 5066888 NO AO 882391 NO A 882391 NO B 171671 NO C 171671 PT A 87624 PT B 87624 US A 5211930	15-04-1992 07-03-1995 22-12-1988 23-04-1992 31-05-1988 02-12-1988 03-01-1994 29-11-1989 18-03-1992 01-12-1992 19-12-1988 22-06-1993 31-05-1988 02-12-1988 11-01-1993 28-04-1993 01-06-1988 30-09-1992 18-05-1993